Study of NbN ultra-thin films for THz hot-electron bolometers

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***Abstract*— Hot-electron bolometer (HEB) mixers based on superconducting ultra-thin *NbN* films are largely used for THz spectroscopy for space and ground-based observations. Performance of the HEB mixers directly depends on the details of the structure and composition of thin film surface, as well as the nitrogen composition and its depth distribution. In this work, we present the study of the composition and the surface oxidation state of *NbN* films grown at two different temperatures and of 5 and 10 nm thickness.**

***Index Terms*—Hot-electron bolometers, NbN, surface analysis, thin films**

I. Introduction

HOT-ELECTRON bolometer (HEB) mixers based on superconducting ultra-thin *NbN* films are largely used for THz spectroscopy for space and ground-based observations [1], [2], [3]. The performance of the HEB mixers directly depends on the details of the structure and composition of the thin-film surface, as well as the nitrogen composition and its depth distribution.

The composition of the *NbN* film affects its superconducting transition critical temperature and width of the transition. Besides the effect on the superconducting critical temperature itself, deviation from the stoichiometric *NbN* composition causes an increase of the normal resistivity of the film, as well as the precipitation of the second phases. At its interface with the substrate, the *NbN* film composition can be affected by the substrate material. It is natural to expect the effect of the substrate material to be dependent on the temperature, at which the *NbN* film was grown. Keeping in mind that the *NbN* films are ultra-thin, typically 5 nm thick, one could expect that, if present, the effect of the substrate material on the *NbN* stoichiometry manifests differently for films with different thicknesses. From the other side, at the outer surface of the film, a natural oxide layer is unavoidable when films are exposed to air. The latter eventually provides additional and unwanted series resistance to the bolometer device, thus, the knowledge about the thickness and composition of the natural oxide layer over the *NbN* film is much desired.

In this work, we present the study of the composition and the surface oxidation state of *NbN* films grown at two different temperatures and of 5 and 10 nm thickness.

II. Experiment

The NbN ultra-thin films were deposited on (100)-Si substrates by means of DC magnetron reactive sputtering of *Nb* in the N_2-containing atmosphere using an AJA Orion-6UD sputtering system. The system is evacuated by a turbo pump and equipped with a load-lock thus achieving base pressure of $< 2\times10^{-8}$ Torr. The 99.95% Nb 2-inch diameter magnetron is placed about 10 cm away from the substrate and slightly off-centered and tilted from the normal to the substrate table [4], allowing highly uniform, < 2% variation, deposition rate across the 4-inch substrate table. The substrate holder was pre-heated to either 650°C and maintained at this temperature during the sputtering (further referred as hot deposition) or kept at ambient temperature during the deposition (further referred as cold deposition). The deposition rate was kept about 1.2 *Å/s*. The further details on the deposition process are reported in [5], [6].

Thin film were analysed with a help of X-ray Photoelectron Spectroscopy (XPS) and Reflected Electron Energy Loss Spectroscopy (REELS). For the studies, the sources of primary electrons (Kimball Physics EMG 4212 with *BaO* cathodes), and X-rays (SPECS XR-50) were employed. Electron energy spectra have been recorded using semi-spherical energy analyzer SPECS Phoibos 225 with absolute energy resolution of 0.3 eV within 0-15 keV range. The *NbN* films have been studied by means of X-ray Photoelectron Spectroscopy (XPS) and Reflected Electron Energy Loss Spectroscopy (REELS).

III. Results and Discussion

With XPS, we studied the oxidized layers at the *NbN* films surface; the sort of the oxides and their thicknesses were identified. Fig. 1 presents XPS spectra recorded on the studied *NbN* films. The recorded spectra are represented as a superposition of the peaks of *Nb* 3p3/2, *Nb-O* and *Nb-N* bonds. From that, one can conclude that metallic niobium is not present in the *NbN* film samples. The eventually residual

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Nb 3p3/2 peak seen for the 5nm film deposited on the hot substrate (Fig. 1a) is likely an artefact of the CasaXPS software extracting individual peaks out of the measured superimposed spectrum [7].

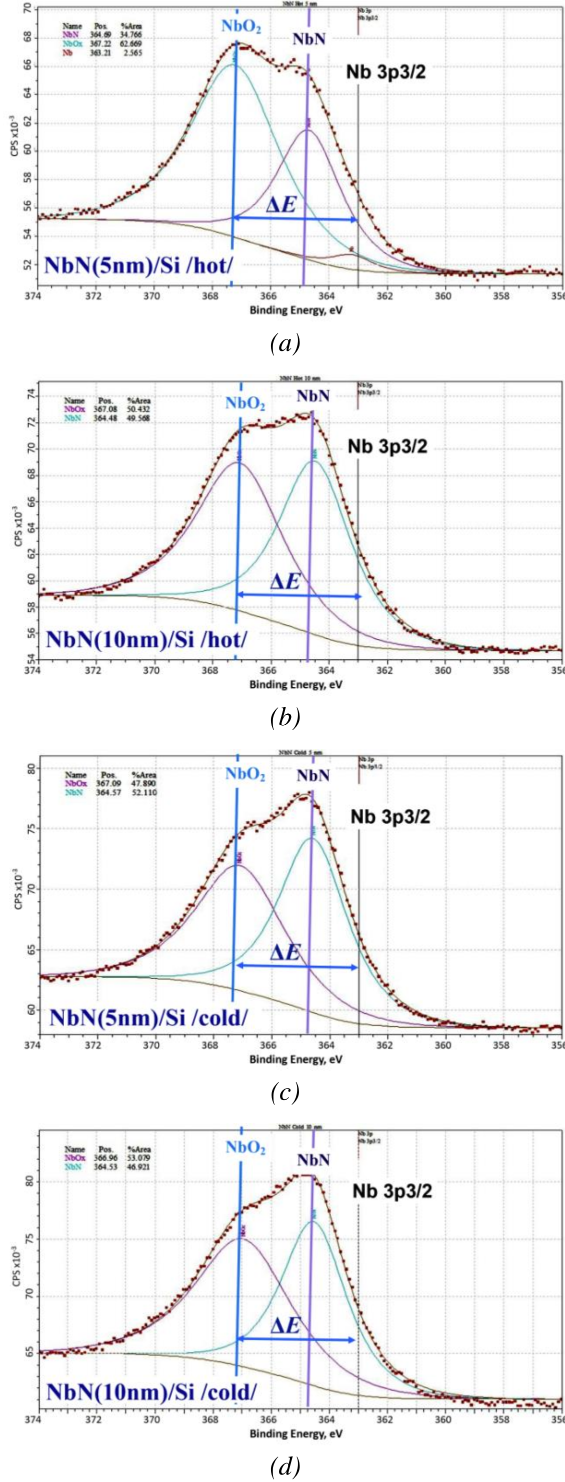

Fig. 1. XPS spectra, recorded on the *NbN* films. Dots represent experimental data; solid lines show results of representation of the spectrum as a superposition of the peaks of *Nb* 3p3/2, *Nb-O* and *Nb-N* bonds (CasaXPS software). (a) – 5 nm *NbN* film deposited on the hot substrate; (b) – 10 nm *NbN* film deposited on the hot substrate; (c) – 5 nm *NbN* film deposited on the cold substrate; (a) – 10 nm *NbN* film deposited on the cold substrate.

The shift *ΔE* (Fig 1a-d) of the *Nb-O* peak position in respect to the position of the *Nb* 3p3/2 peak gives the stoichiometry of the natural oxide [8] at the *NbN* film surface. The observed identical position of the *Nb-O* peaks for all four films indicates the identical composition of the natural oxide films on top of the *NbN*.

Accounting for the peak intensity ratio for NbN and Nb-O, I_{Nb-O}/I_{Nb-N} , allows the evaluation of the oxide film thickness:

$$d_{NbO_x} = \cos(\gamma)\,\lambda_{in_{NbO_2}} \ln\left(\frac{I_{NbO_2}}{I_{NbN}}\frac{\lambda_{in_{NbN}}}{\lambda_{in_{NbO_2}}} + 1\right),$$

where λ_{in} is inelastic mean free path (IMFP) calculated following [9], $\gamma = 54.74°$ angle between the X-ray beam and the direction towards the energy analyzer. The data on the stoichiometry and thickness of the natural oxide films are summarized in the Table I.

TABLE I STOICHIOMETRY AND THICKNESS OF NBO_X FILMS

Sample	*ΔE*, eV	Oxide composition	Oxide Thickness, nm
Nb	4.9	Nb_2O_5	1.5
NbN 5 nm, cold substrate	4.1	NbO_2	0.9
NbN 5 nm, hot substrate	4.0	NbO_2	0.6
NbN 10 nm, cold substrate	4.1	NbO_2	0.5
NbN 10 nm, hot substrate	4.1	NbO_2	0.6

Fig. 2 presents the REELS spectra recorded for *NbN* films, as well as for thick Nb film and reference spectra from [10]. Comparing the REELS spectra for the *NbN* films of different thickness and grown on hot and cold substrates, one can see that the *NbN* plasmon peaks appear at the same electron energy loss. This confirms that the stoichiometry for all *NbN* films is identical for all deposition conditions. One can also extract concentration of the valent electron n_e from REELS data. Energy of electron plasmon oscillation ε_p is defined by the concentration of valent electrons n_e:

$$\varepsilon_p = \hbar e\sqrt{\frac{n_e}{m_e\epsilon_0}}$$

where m_e – electron mass, $\hbar$ - Planck constant, ϵ_0 - permittivity of free space.

The extracted valent electrons concentration in the studied *NbN* films and thick *Nb* film as reference, as well as in their natural surface oxides are summarized in the Table II.

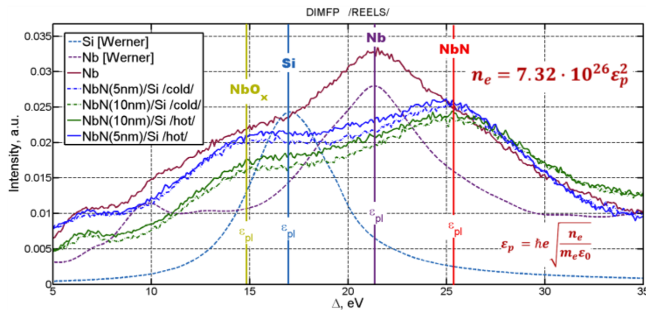

Fig. 2. Differential inelastic scattering cross sections (differential inverse mean free path, DIMFP) extracted by Tougaard method [11].

TABLE II CONCENTRATION OF VALENT ELECTRONS IN NB, NBN FILMS AND THEIR SURFACE OXIDES

Sample	$n_e, 10^{29}$ m^{-3}		
	Nb	*NbN*	*NbO$_x$*
Nb	3.38±0.16	-	1.4±0.6
NbN 5nm, cold substrate	-	4.7±0.4	1.6±0.6
NbN 5nm, hot substrate	-	4.7±0.4	1.6±0.6
NbN 10nm, cold substrate	-	4.7±0.4	1.5±0.6
NbN 10nm, hot substrate	-	4.7±0.4	1.5±0.6

IV. CONCLUSION

We have studied the composition and the surface oxidation state of *NbN* films grown at elevated and ambient temperatures and of 5 and 10 nm thickness. We have found that all the studied films have identical stoichiometry, with no dependence on layer thickness. All studied films do not contain metallic *Nb*, so the nitridation is complete; no evidence of any second phase has been found. Stoichiometric composition and thickness of oxidized surface layer has been identified. For all NbN films, the natural oxide layer consists of NbO_2, in contrast to the one formed on Nb film, which contains Nb_2O_5 oxide. The concentration of valent electrons in *NbN* films and their oxide layers have been extracted from REELS data.

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